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SENSITIVENESS TO DETONATION OF TRINITROTOLUENE AND TETRANITROMETHYLANILIN

BY

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SENSITIVENESS TO DETONATION OF TRINITROTOLUENE AND TETRANITROMETHYLANILIN.

By **Guy B. Taylor** and **Willard C. Cope.**

INTRODUCTION.

The tendency in the development of the modern blasting cap is toward partial replacement of the hitherto exclusively used mercury fulminate by other explosive substances. At present the practice is largely to superimpose a small charge of fulminate, its chlorate mixtures, or lead hydronitride, upon organic nitro compounds or nitrates in the detonator shell. The detonator is usually of the "reinforced" type, (fig. 1) in which an inner perforated shell is pressed down over the charge. The sensitive fulminate composition, fired by fuse or electrically, detonates the secondary explosive, thereby transmitting the impulse that causes the blasting explosive to detonate.

This plan of superimposing an initial primer upon a secondary explosive in a detonator shell offers an excellent arrangement, not only for practically working out the best combination for commercial detonators, but for studying theoretically the process involved in the transmission of the detonating wave from the initial primer to a secondary explosive, and has been used by several investigators.[a]

USUAL METHOD OF PERFORMING DETONATION EXPERIMENTS.

The experiments are usually carried out by weighing into the copper shell a fixed quantity of explosive (trinitrotoluene, pricric acid, guncotton, or the like), and varying the weight of primer until the minimum quantity required for certain detonation is ascertained. It is obvious that the method may be used either to compare the relative sensitiveness of explosives toward the same primer, or the relative efficiencies of different priming compositions in detonating the same explosive.

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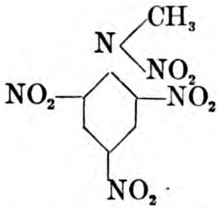
[a] See Wöhler, L., and Matter, O., Beitrag zur Wirkung der Initialzündung von Sprengstoffen: Ztschr. ges. Schiess- u. Spreng-stoffw., Bd. 2, 1907, pp. 181, 203, 244, 265; Martin,—, Über Azide und Fulminate, Darmstadt, 1913. Storm, C. G., and Cope, W. C., The sand test for determining the strength of detonators: Tech. Paper 125, Bureau of Mines, 1916, pp. 1–64.

CHARACTER OF EXPLOSIVES USED IN PRESENT INVESTIGATION.

In the present investigation, which was conducted in the explosives chemical laboratory of the Bureau of Mines at Pittsburgh, the object was to study the action of initial primers.

Two explosives varying fairly widely in sensitiveness to detonation were selected for this work, namely, trinitrotoluene and trinitromethylnitramine. Trinitrotoluene, symmetrical trinitromethylbenzene, $C_6H_2CH_3(NO_2)_3$, is known as an explosive under a variety of names—trotyl, trinol, trilite, tritolo, or TNT. The latter term is used in this paper. Trinitromethylnitramine has the structural formula



and is generally known as tetranitromethylanilin,[a] or more simply tetryl. The latter term is used in this paper.

SENSITIVENESS OF TNT AND OF TETRYL AS DETERMINED BY OTHER INVESTIGATORS.

Will[b] has reported the relative sensitiveness to blow of a number of explosives. The height of drop necessary for a 2-kilogram weight to cause detonation of TNT in an impact machine varied from 57 to 90 cm., depending on the physical condition of the explosive; for tetryl the height was 40 to 65 cm.

According to a report by the Rheinische Westfälische Sprengstoff A. G.,[c] the following minimum charges for detonation of 1 gram of the nitro compounds in reinforced detonator shells 45 by 6.85 mm. were obtained.

Minimum weight of various charges required for certain detonation of TNT and of tetryl.

Charge.	TNT.	Tetryl.
Mercury fulminate............grams..	0.35	0.40
Mercury fulminate, 80 per cent .do.... Potassium chlorate, 20 per cent .do....	.30	.20
Lead hydronitride.............do....	.08	.01

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[a] See Escales, R., Die Explosivstoffe, Ht. 6, 1915, p. 368.

[b] Will, W., Zur Frage der Prüfung von Sprengstoffen auf Transportsichenheit: Ztschr. ges. Schiess- u. Spreng-stoffw., Bd. 1, 1906, p. 209.

[c] See Stuart, A. J., Lead hydronitride (translation): U. S. Artillery Jour., vol. 41, 1914, pp. 212–223.

Martin[a] has also determined the minimum charge of several primers required to detonate these two explosives. A loading pressure of 1,100 kg. per square cm. was used in the reinforced detonator. The results of Martin's determinations follow.

Results of Martin's determinations of minimum charges required to detonate nitro compounds.

Charge.	TNT.	Tetryl.
Mercury fulminate............grams..	0.36	0.29
Silver fulminate................do....	.095	.02
Cadmium fulminate............do....	.11	.008
Mercurous hydronitride.......do....	.145	.045
Silver hydronitride.............do....	.07	.02
Lead hydronitride..............do....	.09	.025
Cadmium hydronitride........do....	.04	.01

It will be noted that Martin's results show a wide range in the efficiency of various initial primers but that tetryl was more sensitive than TNT in every case.

According to Giua,[b] tetryl when fused with TNT makes the latter explosive more powerful and at the same time more sensitive. It is claimed that an addition compound is formed between the two as shown by thermal analysis.

AUTHORS' METHOD OF PREPARING EXPLOSIVE MIXTURES TESTED.

In the author's experiments the mixtures of tetryl and TNT were made by fusing together the two substances and obtaining careful cooling curves. The cooling curves were obtained from different masses of melt and under widely different rates of cooling, but the authors were unable to confirm Giua's conclusion that an unstable compound of three molecules of TNT to two of tetryl is formed. The tendency of the melts to supercool was great, and the heat effects of the crystallization were so small as to render methods of thermal analysis untrustworthy.

The TNT used was an imported sample of high purity known in the Bureau of Mines laboratory under the number M–1789. The tetryl (M–1849) was crystallized once from benzene, and melted sharply at 129.2° C., uncorrected. Mixtures containing 10, 20, 40, and 50 per cent of tetryl were made by fusion in a water bath, the solid resulting on cooling being ground in a mortar. The minimum charge of primer consisting of 90 parts of mercury fulminate and 10 parts of potassium chlorate necessary for complete detonation was determined for each mixture except that containing 40 per cent tetryl.

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[b] Data obtained from Stettbacher, A., Altes und Neues über Initialzundstoffe: Ztschr. ges. Schiess- u. Spreng-stoffw., Bd. 9, 1914, p. 355.

[a] Giua, M., Die Industrie des Trinitroluols in Italien und deren Entwicklungsbedingungen: Ztschr. ges. Schiess- u. Sprengstoffw., Bd. 10, 1915, p. 109; Miscugli di explosivi nitrati e nitrazione del toluene; Gaz. chim. Ital., t. 45, pt. 2, July 18, 1915, pp. 32–44.

METHOD OF USING SAND TEST.

The "sand test" as developed by Storm and Cope[a] for the direct testing of detonators offers a most useful and convenient method for the laboratory study of priming compositions. In this test the detonator is buried in the center of 100 grams of "Ottawa standard sand" contained in a cylindrical chamber, approximately 15 cm. deep and 3.1 cm. in diameter, bored out of a steel block. The sand is practically pure quartz, passes entirely through a 20-mesh screen, and is held on a 30-mesh screen. The grains from different lots are of remarkably uniform size. After the detonator has been fired the sand is screened, and the quantity passing through a 30-mesh screen is regarded as a measure of the strength of the detonator. In a long series of tests Storm and Cope found that the result given by the "sand test" was a definite function of the weight of the charge and that the quantities of sand crushed by mercury fulminate and its chlorate mixtures was comparable to their relative efficiencies in causing complete detonation of nitro substitution compounds. The test is an accurate indication of the grade of commercial detonators. Most other direct tests, such as the lead-plate test, are not quantitative, or depend upon effects not easily or accurately measured.

DETAILS OF EXPERIMENTS.

The tests with TNT, tetryl, and their mixtures were carried out as follows: Exactly 0.4 gram of the explosive was weighed into a copper shell 5 mm. in diameter and slightly pressed with a neatly fitting glass rod having a flat end. The primer, 90 per cent mercury fulminate and 10 per cent potassium chlorate, was placed on top, and the thin copper reinforcing cap (9 mm. long with 2.3-mm. perforation) was inserted and pressed down into the shell for one minute under a loading pressure of 200 atmospheres per square inch (206 kg. per square cm.). A short piece of fuse was crimped into the shell, and the detonator fired in the sand bomb. The results of the individual shots are given in the table following:

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[a] Storm, C. G. and Cope, W. C., The sand test for determining the strength of detonators: Tech. Paper 125, Bureau of Mines, 1916, 68 pp.

***Results of sand tests** of 0.4000-gram mixtures of trotyl and TNT with varying weights **of** fulminate-chlorate (90 : 10) primer in reinforced detonators.*

Explosive mixture.	Weight of primer, grams.								
	0.32	0.25	0.24	0.23	0.22	0.21	0.20	0.19	0.18
	Weight of sand pulverized finer than 30-mesh, grams.								
100 per cent TNT and 0 per cent tetryl	37.5	34.4							
	38.0	34.7							
	37.6	34.1	[a] 13.2	[a] 13.9					
	37.8	35.1							
	37.3	33.8							
	[b] 37.6								
90 per cent TNT and 10 per cent tetryl					31.6	25.0			
					30.1				
	38.0		30.6		32.3	[a] 13.4	[a] 13.8		
					27.8				
					28.6				
80 per cent TNT and 20 per cent tetryl						27.0			
						28.7			
	39.0				34.1	32.3	[a] 11.2		
						33.3			
						32.0			
50 per cent TNT and 50 per cent tetryl							31.5		
							29.4	29.2	
	39.9						30.7	[a] 10.8	[a] 12.9
							27.5		
							29.3		
0 per cent TNT and 100 per cent tetryl								34.9	
								36.0	35.5
	[b] 41.5	39.7					39.1	33.4	33.5
								33.5	[a] 5.4
								32.5	

[a] **Incomplete detonation.**

[b] Average of five shots.

COMMENTS ON RESULTS.

In every case of incomplete detonation as indicated by a small crushing effect, a part of the charge unexploded was found in the sand. The criterion of the minimum charge was five complete detonations with no failures. The minimum charges of fulminate-chlorate (90 :10) primer that caused complete detonation of the different mixtures of explosive, as shown by the preceding table, were as follows:

Minimum charges of fulminate-chlorate (90 : 10) primer that caused complete detonation of different mixtures of explosive.

Explosive.		Smallest weight of primer that caused complete detonation of explosive.
TNT.	Tetryl.	
Per cent.	*Per cent.*	*Gram.*
100	0	0.25
90	10	.22
80	20	.21
50	50	.20
0	100	.19

Besides the mixtures made by fusing the TNT and the tetryl a mixture containing 20 per cent tetryl and 80 per cent TNT was made by mechanically mixing the finely ground constituents. The minimum charge of primer that caused complete detonation of this mixture was 0.21 gram, or the same as that for the fused mixture. It would seem unnecessary to assume the existence of a compound between the two substances to account for the increase of sensitiveness of their mixtures. The results with a priming charge of 0.32 gram indicated a slight increase of strength with increasing tetryl content.

The sensitiveness of TNT-tetryl mixtures to moist fulminate mixture was also determined. A number of detonators were made up as above described containing charges of 0.4 gram base charge and 0.32 gram of 90:10 priming charge. These were stored over water and tested from time to time. The pure TNT failed when the detonator had taken up 0.0030 gram of moisture; 10 per cent tetryl detonated when the moisture content was 0.0037 gram and failed when the moisture content was 0.0048 gram; 50 per cent tetryl detonated when the moisture content was 0.0048 gram and failed when the moisture content was 0.0055; and the pure tetryl cap still detonated with a moisture absorption of 0.0062 gram.

Lead hydronitride, or lead azide (PbN_6), seems to have a distinct preference for detonating tetryl. The authors have found that as little as 1 milligram will often detonate tetryl, and that 0.01 gram will always do so. The minimum charge for TNT under a loading pressure of 200 atmospheres is 0.23 gram; with a pressure of 400 atmospheres it is about 0.15 gram. Martin found the minimum charge to be 0.09 gram under a loading pressure of about 1,000 atmospheres.

CONCLUSIONS.

TNT (trinitrotoluene) is much less sensitive to detonation than tetryl (trinitromethylnitramine, or tetranitromethylanilin). The sensitiveness of the former is increased by admixture of the latter. These two compounds, varying widely in sensitiveness, are suitable substances on which to test the efficiency of initial priming compositions. In Bureau of Mines reports that are to follow, the relative efficiencies of various mixtures of mercury fulminate and other substances in detonating these two compounds will be given.

NOTE.

On account of the present high price of mercury used in the manufacture of mercury fulminate, detonators have greatly advanced in price. Manufacturers are seeking a substitute to partly replace the fulminate. By use of a suitable base charge and of a fulminate-chlorate mixture as a primer in the reinforced detonator about one-half as much fulminate is required for a cap of given strength. Commercial blasting caps have been manufactured containing both TNT and tetryl as the base charge. About 0.40 gram of base charge and 0.32 gram of 90:10 fulminate-chlorate primer make a cap of the No. 6 grade. It is important to use as a factor of safety about 50 per cent excess primer above the minimum quantity required for complete detonation of the base charge. It is also important to use a base charge not too insensitive to slightly moist fulminate. Any explosive proposed for use as a base charge should be thoroughly tested to meet any possible conditions of treatment or storage to which the blasting caps are likely to be exposed in practical work, for the failure of a single cap may be a serious matter. On account of its insensitiveness to slightly moist fulminate TNT has proven an unsatisfactory base charge.

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BULLETIN 17. A primer on explosives for coal miners, by C. E. Munroe and Clarence Hall. 61 pp., 10 pls., 12 figs. Reprint of United States Geological Survey Bulletin 423.

BULLETIN 59. Investigations of detonators and electric detonators, by Clarence Hall and S. P. Howell. 1913. 73 pp., 7 pls., 5 figs.

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BULLETIN 80. A primer on explosives for metal miners and quarrymen, by C. E. Munroe and Clarence Hall. 1915. 125 pp., 15 pls., 17 figs.

BULLETIN 96. The analysis of permissible explosives, by C. G. Storm. 1916. 88 pp.

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TECHNICAL PAPER 12. The behavior of nitroglycerin when heated, by W. O. Snelling and C. G. Storm. 1912. 14 pp., 1 pl., 2 figs.

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TECHNICAL PAPER 125. The sand test for determining the strength of detonators, by C. G. Storm and W. C. Cope. 1916. 68 pp.

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